

IDENTIFICATION OF ICE VI ON THE HUGONIOT OF ICE I<sub>h</sub>

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**Abstract.** Ice VI has been produced by shock compression of ice I<sub>h</sub> to about 2 GPa. This is the second high-pressure polymorph of water observed in shock loading. These experiments point out the ease with which high-pressure phases can form when ice I<sub>h</sub> is impacted. The new shock data, combined with previous static measurements, provide preliminary equation of state parameters for ice VI of

$$V_o = 0.7732 \text{ m}^3/\text{Mg}, K_o = 10.7 \text{ GPa}, \\ (dK/dP)_{P=0} = 7.3, \\ \alpha = 1.1 \times 10^{-4} \text{ K}^{-1}, \text{ and } C_v = 2.2 \text{ kJ/kg}.$$

## Introduction

Ice exists in more solid phases than any other simple material. The familiar phase is ice I<sub>h</sub>, with hexagonal symmetry. Ice I refers to ice with density near 0.92 Mg/m<sup>3</sup>. The subscript h is used to distinguish the normal hexagonal structure from a cubic analog formed under unusual circumstances (see Hobbs, 1974, for details). Near 263 K the stable phase between 630 and 2200 MPa is ice VI. Although these pressures are so high that ice VI is unlikely to be an important constituent of the interiors of any planets or satellites (those that are large enough to have pressures of 1 GPa or so are probably so hot as to melt ice VI), it has been suggested that ejecta on ice-covered satellites in the outer solar system contain some ice VI (Gaffney and Matson, 1980). Previous interpretations of the Hugoniot of ice (Anderson, 1968; Larson *et al.*, 1973) have stressed the importance of melting at pressures as low as 200 MPa, although the probable occurrence of ice V at about 700 MPa was reported (Larson *et al.*, 1973). We have obtained a Hugoniot volume at about 2 GPa that is clearly indicative of a high pressure solid phase. When this datum is combined with data at 3.7 GPa from Anderson (1968), the occurrence of ice VI on the Hugoniot of ice I<sub>h</sub> is indicated.

## Experimental Techniques

The observation of ice VI was accomplished using a 40-mm propellant gun to accelerate an aluminum (2024-T351) flyer plate so as to impact a copper buffer plate, upon which a sample of ice I<sub>h</sub> was mounted. The buffer plate also served as part of the vacuum seal

of the target (Fig. 1). It was necessary to enclose the entire sample assembly in a double vacuum system so that frost would not form on the target before the main target chamber and barrel were evacuated, and so that the target would not evaporate after evacuation. This was done by enclosing the vacuum-tight sample assembly in a vacuum-tight plexiglas box as shown in Fig. 1. A 47-mm hole on the front (impact) surface permitted the flyer plate to impact directly on the copper. Prior to evacuation of the main chamber, this hole was sealed with an O-ring and covered with a plexiglas plate, and the subsidiary chamber was evacuated. When the vacuum in the main chamber reached that of the subsidiary chamber, the coverplate fell off, exposing the impact face.

The sample was prepared by pressing crushed ice I<sub>h</sub> (made from distilled water) into the sample chamber using a die to produce the desired surface topography. The sample density was not measured, but visual examination showed it to be optically clear. After pressing, the target was stored below 250 K except when being installed in the plexiglas box or in the target chamber. Target temperatures were kept below 270 K at all times. The sample was cooled in the target chamber by pumping Freon 12 (CCl<sub>2</sub>F<sub>2</sub>) through a coil in an acetone/dry ice bath and then through a coil soldered to the outer edge of the copper buffer plate. After installation the temperature was maintained at 263 ± 0.5 K by raising or lowering the former coil in the bath. Temperature was measured by a thermocouple in the buffer plate. After installation and alignment of the sample assembly in the target chamber, it was visually checked to assure that no gross creep or melting had occurred.

The flyer velocity was determined from the time intervals between extinction of laser beams traversing the projectile path. The measured flyer velocity was 1465 ± 3 m/s, indicating that the copper was shocked to 455 m/s and 16.2 GPa. The time required for shock transit from the rear surface of the buffer to the rear surface of the target was determined from a streak camera record. The particle velocity in ice was obtained by impedance match to the unloading curve with a copper free surface velocity of 911 ± 3 m/s and the observed shock speed.

## Results and Discussion

The observed shock velocity was 2433 ± 32 m/s. Taking the density of ice I<sub>h</sub> at

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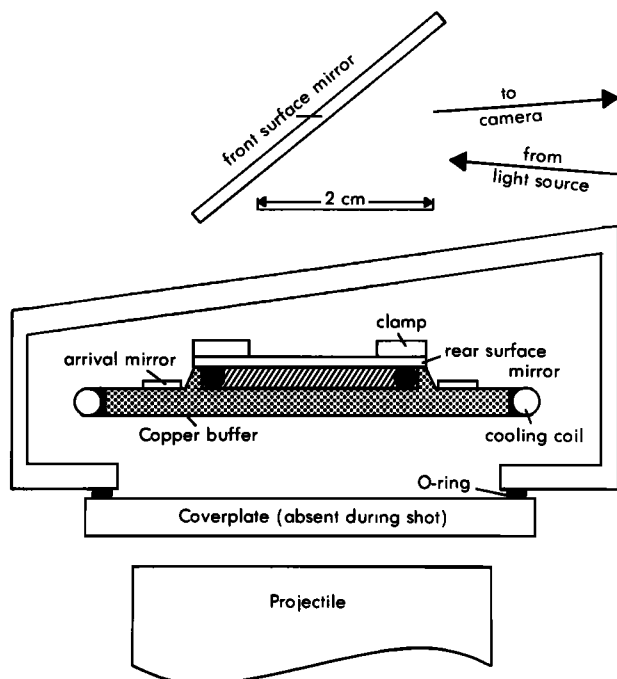


Fig. 1. Schematic experimental arrangement for ice equation of state experiment.

263 K to be  $917 \pm 9 \text{ Mg/m}^3$ , the particle velocity is found to be  $858 \pm 3 \text{ m/s}$  at  $1.91 \pm 0.04 \text{ GPa}$ . These data yield a specific volume of  $0.706 \pm 0.018 \text{ Mg/m}^3$ . This datum is shown in pressure-volume space in Fig. 2. This specific volume is about 10% below the measured Hugoniot of liquid water, firm evidence of the occurrence of a solid phase.

The present datum can be used with Anderson's (1968) two data points near 3.7 GPa (both are shown in Fig. 1) to calculate a Hugoniot curve for ice above 0.8 GPa, assuming a linear relation between shock velocity and particle velocity. That curve is shown by the heavy line in Fig. 2. The 263 K isotherm of ice VI in this figure is fit to three points at 0.0, 0.8, and 2.15 GPa, using the pressure (P)-volume (V) relation of the same form as that which follows from the linear shock velocity-particle velocity relation (Olinger and Halleck, 1975),

$$PV_0^2/(V_0 - V) = C_T + S_T P(V_0 - V), \quad (1)$$

where the zero-pressure volume and  $C_T$  and  $S_T$  are equation of state parameters. A value for  $V_0$  of  $0.7732 \text{ m}^3/\text{Mg}$ , is obtained by adding a thermal correction to the volume at 110 K measured by Bertie *et al.* (1964) assuming that  $\alpha = 1.1 \times 10^{-4} \text{ K}^{-1}$  (volume expansion coefficient), as suggested by Kamb (1969). The point at 0.8 GPa is obtained by applying a similar correction to the volume at 223 K measured by Kamb and Davis (1964). The point at 2.15 GPa was obtained by adding the volume change of  $0.0565 \text{ m}^3/\text{Mg}$  measured by Bridgman (1937) for ice VII+ice VI to the volume of ice VII taken from Olinger and Halleck (1975) with changes in the pressure scale as suggested by Olinger (personal communication),

again with a thermal expansion correction. With these points, it is found that  $C_T = 2880 \text{ m/s}$  and  $S_T = 2.078$ , corresponding to  $\rho_0 = 1293 \text{ kg/m}^3$ ,  $K_0 = 10.7 \text{ GPa}$  and  $K'_0 = 7.31$ . The Hugoniot lies above the ice VI isotherm, but well below the Hugoniot of liquid water at the same pressure (Rice and Walsh, 1957). There is no doubt that the data indicate the presence of a solid phase on the Hugoniot of ice, although the transition may not be complete at 1.9 GPa. Assuming that the transition is complete and using a transition energy of about 70 kJ/kg for ice  $I_h \rightarrow$  ice VI, the data indicate that  $\gamma = 0.7 \pm 0.1$  for ice VI. Using this value of  $\gamma$  and assuming a value of 2.16 kJ/(kg K) for the specific heat of ice VI at constant volume, shock and post-shock temperatures of 400 and 350 K are calculated for Hugoniot states at 1.9 GPa and 600 and 500 K for Hugoniot states at 3.7 GPa, respectively. The specific heat was estimated from infrared spectra in a manner described by Gaffney (1980).

Gaffney and Matson (1980) have suggested that impact ejecta on the cold satellites in the outer solar system may contain high pressure phases (hpp) of ice. Ice hpp's are metastable at temperatures below 125 K (Bertie *et al.*, 1964) and the pressures required to

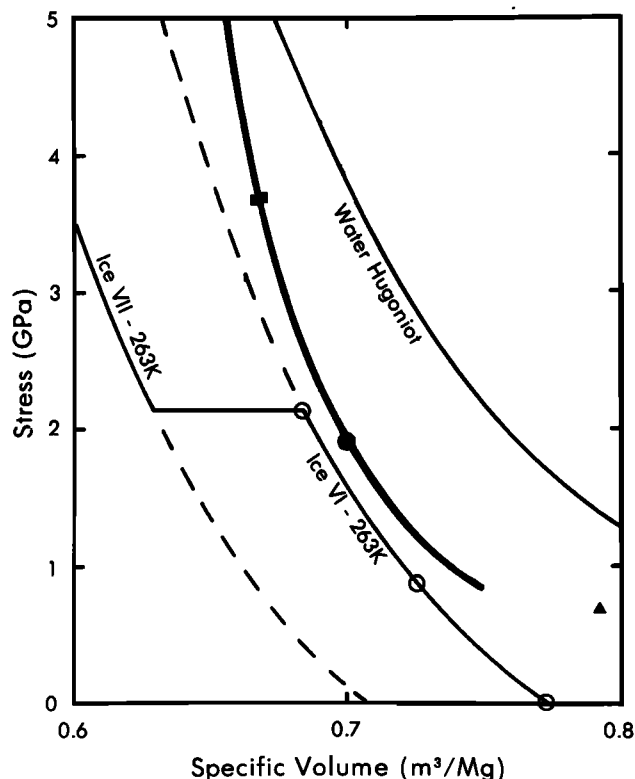


Fig. 2. Hugoniot of ice  $I_h$  shocked from 263 K. Heavy line is linear fit to data of Anderson (1968) (■) and the present datum (●). Larson *et al.* (1973) inferred ice V from their datum (▲). Isotherm of ice VI at 263 K, shown as a light line (dashed where metastable), is fit to data at 0.0, 0.8, and 2.1 GPa (○), as described in text. Ice VII isotherm after Olinger and Halleck (1975). Liquid water Hugoniot from Rice and Walsh (1957).

form them are modest compared to those for silicates, so that post-shock temperatures may be low enough to permit metastable hpp's in icy regoliths. The identification of ice VI and ice V on the Hugoniot of ice  $I_h$  is necessary supporting observations and increase the probability that spectral studies of icy satellites will observe features due to hpp's of ice.

**Acknowledgments.** Supported under NASA Contract NASW-3224. PacTech report number PT-U79-0408. Contribution no. 3345, Division of Geological and Planetary Sciences, California Institute of Technology. We appreciate the experimental assistance of J. Long, E. Gelle, and M. Long in operating the facilities in the Roland and Helen W. Lindhurst Laboratory of Experimental Geophysics and P. L. Riersgard for his assistance in sample preparation.

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(Received January 15, 1980;  
accepted January 28, 1980.)